Dated: October 23, 2001

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UTILITY PATENT APPLICATION TRANSMITTAL

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Assistant Commissioner for Patents BOX PATENT APPLICATION Washington, DC 20231

Sir:

Transmitted herewith for filing is the utility patent application of:

Inventor(s): Chi-Chan CHEN Wei-Chi KII Suno-Kay CHIII Chi-Meno TZENG In melting and refining processes sub- ally feasible but not economic, i.e. because In melting and refining processes substantial quantities of slags are produced. Intensive efforts have been invested and many proposals have been made to utilize such metallurgical slags. Interest has been focused on blast-furnace slags, about which an ample literature is now available, see for example Keil T.F. "Die Hochofenschlacke" (Blastfurnace slag) 2nd edition, Düsseldorf 1963. The use of blast-furnace slags has become

important from an economic point of view especially for the production of cement, but this covers only a minor part of the slag

Slags of a basic nature are obtained in very large quantities especially from steel production. Certain special slags of this type can be used as fertilizers, but for most of the slags there is no method of complete and economic recovery with utilization of the heat of the molten slag. In many cases the aforesaid types of slags include valuable metals, as for example Fe, Cr, Ni, and Mn, but yet they are dumped in slag yards. The slag content of oxides and more or less finely distributed metal is thereby lost. The latter, it is true, is sometimes recovered to some extent. In conventional slag handling a considerable loss is made by not utilizing the

large amounts of heat included in the molten slag, to which loss are to be added the costs for handling the slag and for the

of the high temperatures required.

Some proposals for the treatment of blastfurnace slags suggest the use of containers lined with carbon bricks, because carbon bricks are resistant to reducing slags. Another reason was the desire to use an electrically conductive lining material.

It is also known that in several metallurgical processes the slag composition can be so controlled that the slag subsequent to grinding is directly adapted for use as aluminate cement. It is, however, a decisively restrictive factor for these processes that they require a slag with a high Al₂O₃ content, which, in the furnace, is in equilibrium with the metal being the main object to be achieved by the process.

In the British patent specification 1,229,955 a method for the production of hydraulic cement is proposed, in which reducing gases, preferably carbon monoxide or hydrogen gas, are used (not solid reducing agents), while heat is supplied by an oxidation process. It is apparent that the oxidation process disturbs the reduction process. Also, the desired reduction of manganese from manganese oxide with help of carbon monoxide and/or hydrogen gas at the temperatures indicated can take place only to a small extent.

Finally, one may say that all methods heretofore suggested are not applicable generally

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and do not result in a complete economic recovery of slag.

The present invention provides a method of recovering a metallurgical slag containing metal oxide and, possibly, elementary metal, in which the molten slag is tapped into a container, carbon and material containing silicon or aluminium are added to reduce the metal oxide, the melt being maintained at a temperature preventing foaming while allowing sedimentation of the reduced metal and any elementary metal originally present, and the sediment and melt are separated, lime or aluminium-oxide-containing material being added to the melt in a quantity such as to give it the composition of an oxide mixture suitable for use in Portland cement or aluminate cement.

It is obvious to the expert that a contamination of the residue by, for example, oxides of Fe, Mn and similar colouring metal oxides would prevent the utilization of the residue as an additive to, for example, white cement. A considerable economic advantage is obtained by using as the aluminium containing material, bauxite heavily contaminated with iron oxide; a high-quality aluminate cement results, the iron having separated out during sedimentation.

For carrying out the method, a plant is required which in principle should comprise a reactor vessel, for example the ladle into which the slag is to be tapped, or a stationary container to which the slag or slags are to be transported for treatment. and which comprises a suitable equipment for the supply of heat, when required, which heat may be produced either electrically or by combustion. The plant further includes means for the addition of reducing agents and other additives to the slag. Pre-heating of the additives, which is important for the economy of the method, is ensured either by utilizing available combustible waste gas or by other 45 heat generating installations known per se. The bottom portion of the reactor vessel advantageously is provided with a suitable tapping device for the removal of sedimented metals originating from the process in which

the slag was formed and from the reduction of the slag according to the method of the invention. The plant will also include installations in which the residue (removed slag is caused to solidify at the speeds desired for obtaining a suitable structure and form of

As regards the chemical composition of the metallurgical slags treated according to the invention, the SiO -content normally is above

It is again emphasized that the control of the viscosity during the reduction process is of the highest importance. When, for example, heat is added by the combustion of, e.g., carbon or oil with oxygen, prior to reduction with carbon, the difficulty may arise that the temperature, which ensures the desired fluidity, cannot be held continuously, because the reduction process with carbon consumes heat. The resulting lowering of the temperature brings about foaming. In such a case one operates intermittently, i.e., by the steps of supplying heat, reducing, tapping metal, supplying heat again, and so on, until the residue has the desired composition.

It has been found that the method according to the invention is advantageous for processing or regenerating (refining) waste products which contain metallic substances in the elementary state or in the form of chemical compounds, such as grindings, waste products, from the chemical industry, heavily contaminated metals scale, neutralization products, dross, etc. These waste products are added to the slag prior to reduction.

The method according to the invention is of general applicability, and its complete exemplification would be unusually extensive. In the following, therefore, only some examples are given to illustrate the main features of the invention.

In the Examples, "/ refers to " by weight.

Example 1.

In a lined ladle, 20 tons of a basic steelmaking slag were tapped, having a temperature of 1600 C and the following composition:

AgO MnO PO FeO SiO. Al O CaO 2.5 / $1.5 \ /$ 1.7 $16 \, \text{//}$ **50** %

In addition, the slag contained 10 ' 100 metallic iron. The ladle was placed under an arc furnace roof, and the slag was reduced by the addition of fine-grained petroleum coke and the supply of electrical energy. In 105 order to avoid excessive expansion of the slag it was necessary to heat the slag to a temperature at which it was sufficiently fluid. At the same time bauxite (71% Al O , 4 SiO, 23 / FeO) preheated to 1000°C was 110 added. The bauxite was preheated in a shaft

placed above the furnace roof, where the waste gases from the reduction were burned. The reduction was completed with an addition of aluminium metal.

The total additions during a treatment time 115 of 70 minutes were 1.3 tons of coke, 10.1 tons of preheated bauxite, and 1.2 tons of aluminium, 4.4 MWh of electrical energy were supplied.

On tapping 8.1 tons of metal (spiegeleisen) 120 were obtained, having a composition of 12

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Mn, 11% Si, and 1.6% P. Furthermore, a residue of 23 tons was left, having the following composition:

CaO SiO₂ Al O₃ MgO S 5 44.6% 7.67 45.0% 2.2% 0.1%

The residue was teemed into moulds,

cooled slowly and ground to the fineness of cement. The values of compression strength corresponded to those of high aluminate cement.

Example 2.

A liquid basic steelmaking slag having the following composition:

CaO SiO₂ Al₂O₃ MgO FeO MnO P₂O₂ 49% 16% 1.5% 6.5% 15% 6% 1.5%

was reduced with carbon.

During the reduction bauxite (60% Al₂O₂, 17% SiO₂, 20% FeO) preheated to 1000°C was added (as the aluminium-containing material) and furthermore SiO₂ in the form of sand (as the silicon-containing material).

There was added, per ton of treated slag: 280 kg preheated bauxite and 63 kg sand,

 $\begin{array}{cccc} \text{CaO} & \text{SiO}_{\pm} & \text{Al_2O}_{\pm} & \text{MgO} \\ 44.2\% & 27.5\% & 16.2\% & 7.4\% \end{array}$

The granulate after grinding to the fineness of cement showed excellent hydraulic properties. Thus, with activation of only 20%, portland cement and with 4%, gypsum added, values of compressive strength after 3, 7, and 28 days were measured which were 40 at maximum only 8% less than the corresponding values for pure portland cement.

Example 3.

In a modification of the process according to Example 2, the slag temperature was increased towards the end of the reduction process to over 1600°C, and the reduction completed by introduction of aluminium metal. The resulting granulated slag then contained

CaO SiO Al₂O₃ 44.2% 38% 10%

and 4.9 kg carbon; 203 kWh of electrical energy were supplied. There was obtained per ton of slag 290 kg spiegeleisen with 14%, Mn, 2%, Si, and 1.3%, P; and 1040 kg of residue.

The residue was granulated with water from a slag temperature of 1560°C and had the following composition:

only 0.1% FeO and 0.1% MnO and was completely white.

On activating the ground granulate with 20% of conventional white cement, a cement was obtained which remained white also under hydration and did not show the blueblack colouring that normally occurs under hydration of cements containing blast furnace cement.

Example 4.

A basic steelmaking slag according to Example 2 was tapped into a stationary furnace together with the same quantity of blast furnace slag, having the following composition.

MgO S Alkali 6% 1.3% 1.5%

The reduction was performed according to Example 2 with the exception that no sand was added.

The residue had the following composition:

CaO SiO₂ Al₂O₃ MgO S Alkali 44.1% 30% 13.1% 6.7% 0.7% 0.8%

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1. A method of recovering a metallurgical slag containing metal oxide and, possibly, elementary metal, in which the molten slag is tapped into a container, carbon and material containing silicon or aluminium are added to reduce the metal oxide, the metal being maintained at a temperature preventing foaming while allowing sedimentation of the reduced metal and any elementary metal originally present, and the sediment and melt are separated, lime or aluminium-oxide-contain-

ing material being added to the melt in a quantity such as to give it the composition of an oxide mixture suitable for use in Portland cement or aluminate cement.

2. A method as claimed in claim 1, in which lime is added to the melt to give it a composition suitable for use in Portland cement, the material containing silicon or aluminium comprising elementary silicon or aluminium,

3. A method as claimed in claim 1 or 2, in which, before reduction of the slag, one